TETRALIN HYDROPEROXIDE

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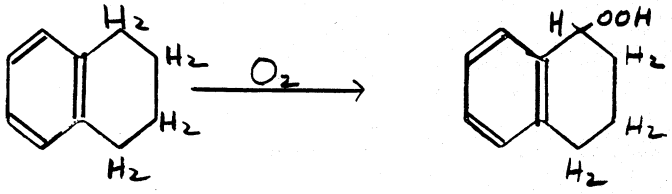
(Hydroperoxide, (1,2,3,4-tetrahydro-1-naphthyl)-)



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1. Procedure

In a 1-l. round-bottomed three-necked flask, equipped with a thermometer, a reflux condenser, and two fritted-glass gas dispersion tubes (Note 1), is placed 600 g. (4.54 moles) of pure tetralin (Note 2). The flask is placed in a constant-temperature bath at 70°, and a finely dispersed stream of oxygen is passed through the tetralin until the peroxide content of the reaction mixture is 25-30% as shown by an active oxygen content of 2.4-2.9% (Note 3). This oxidation requires 24-48 hours. The reaction mixture is then distilled (Note 4) in an all-glass apparatus at 0.2-0.4 mm. through a 60 by 2.5 cm. Vigreux column, until a pot temperature of 70° is reached. About 370-380 g. of unoxidized tetralin, boiling at 32-45°/0.2-0.4 mm., is recovered. The pot residue is a slightly viscous amber-colored oil which weighs 225-235 g. and consists of about 80% tetralin hydroperoxide (Note 5). To obtain the pure hydroperoxide the residue is dissolved in 450 ml. of toluene and the solution is cooled to -50° with stirring (Note 6). After standing at -50° for 1 hour, the slurry is separated by suction filtration (Note 7) and the precipitate is dried at room temperature at 1-2 mm. There is thus obtained 120-125 g. of moderately pure tetralin hydroperoxide, m.p. 50.2-52.0°, active oxygen content 9.20% (Note 8). Recrystallization from 480 ml. of toluene at -30° yields 80-85 g. (44-57% yield based on the peroxide content of the oxidized tetralin) of pure tetralin hydroperoxide as a colorless solid, m.p. 54.0-54.5°, active oxygen content, 9.70% (Note 9).

2. Notes

1. Rubber connections must be avoided because rubber is rapidly attacked by tetralin. Convenient gas dispersion tubes are Pyrex No. 39533.

2. Pure tetralin was prepared from the practical grade supplied by the Eastman Kodak Company by the procedure of George and Robertson.[2] Three kilograms was fractionally distilled through a packed column, the fraction boiling at 204-207° being retained (2.7 kg). This was gently shaken with 1 lb. of mercury, and the upper layer was carefully decanted through fluted filter paper. The crude tetralin was next shaken with saturated aqueous mercuric acetate solution, and the aqueous layer and a small amount of orange precipitate were discarded. The hydrocarbon was then shaken with 5 successive 300-ml. portions of concentrated sulfuric acid, once with 10% sodium hydroxide, and finally with water until the washings were neutral. The tetralin was dried over anhydrous calcium chloride and distilled through a packed column in a nitrogen atmosphere. In this way, 2 kg. of pure tetralin was obtained, b.p. 206-207°, n_D^{20} 1.5428.

3. Active oxygen content is determined iodometrically:[3] In an iodine flask, an accurately weighed sample (0.1-0.3 g.) is dissolved in 20 ml. of an acetic acid-chloroform solution (3:2 by volume), and 2 ml. of saturated aqueous potassium iodide solution is added. The flask is immediately flushed with nitrogen, stoppered, and allowed to stand at room temperature for 15 minutes. Fifty milliliters of water is then added with good mixing, and the liberated iodine is titrated with 0.1 N sodium thiosulfate, employing starch as indicator. A blank titration, which usually does not exceed 0.2 ml., is also run. One milliliter of 0.1 N sodium thiosulfate is equivalent to 0.00821 g. of tetralin hydroperoxide.

4. The distillation should be conducted behind a safety shield.

5. Peroxide loss up to this point is negligible provided an all-glass apparatus has been used throughout and the distillation temperature has not exceeded 70°.

6. A Dry Ice-ethanol bath is convenient for cooling the solution.

7. Filtration may be carried out in a suction funnel surrounded by a Dry Ice-ethanol cooling bath, or using a cold box maintained at -50°.

8. Pure tetralin hydroperoxide has an active oxygen content of 9.75%.

9. Tetralin hydroperoxide is a convenient model compound for many studies in peroxide chemistry. It remains colorless and does not decrease in peroxide content for months if stored in the dark at or below 0°. Storage under warm summer conditions for several months results in decomposition to a dark, viscous liquid.

3. Methods of Preparation

The present procedure is adapted from that reported by Hartmann and Seiberth[4] and Hock and Susemihl.[5] Robertson and Waters[6] employed cobalt naphthenate as a catalyst, but this is not required.

1 Eastern Regional Research Laboratory, U. S. Department of Agriculture, Philadelphia, Pennsylvania.

2 George and Robertson, Trans. Faraday Soc., 42, 227 (1946).

3 Wheeler, J. Am. Oil Chemists' Soc., 9, 89 (1932).

4 Hartmann and Seiberth, Helv. Chim. Acta, 15, 1390 (1932).

5 Hock and Susemihl, Ber., 66, 61 (1933).

6 Robertson and Waters, J. Chem. Soc., 1948, 1578.